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UNIFIED METHODS FOR THE ANALYSIS OF FATTY MATERIALS

INTERNATIONAL UNION OF CHEMISTRY

THIRD REPORT
OF THE INTERNATIONAL COMMISSION FOR THE STUDY OF FATTY MATERIALS
(Publication honored by a grant from U. N. E. S. C. O.)
1948

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Agricultural Research Administration
Bureau of Agricultural and Industrial Chemistry

January 25, 1949

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Unified Methods for the Analysis of Fatty Materials
International Union of Chemistry
Third Report -- 1948

METHOD 1. OLEAGINOUS SEEDS

(a) Recommendations concerning the sample. To permit a correct analysis, samples of large seeds such as coconut, shea, etc., and of medium size seeds such as palm kernel, peanut and soya should weigh from 2 to 5 kilos, and of small seed such as flax, rape and sesame the sample should weigh at least 200 grams.

(b) Conditions of analyses. The moisture and oil contents shall be expressed as a percentage of the original sample containing any impurities present in it. To satisfy the demands of some parties these values may be indicated for the pure seed sample. Depending on the circumstances the chemist will conduct the determinations on the original sample or on the pure seed sample after separating the impurities by screening or sorting.

In the latter case he will calculate the percentages of moisture and oil in the original seed sample by taking into account the percentages of impurities. Separate determinations will be conducted on the impurities for moisture and oil that they may contain and the results taken into account in the final calculation of the results for the original sample.

When the sample contains foreign oleaginous seed, the analyst will, according to the provisions of the contract, determine oil on these seeds separately.

When acidity of the oil is requested, the analyst who extracts the oil from the different fractions (pure seed, impurities, and foreign seed) should take into account the different acidities observed on these fractions in making the final calculations on the original sample.

Whether the impurities have been separated or not, the analyst will mix the sample carefully in order to make it homogeneous, and after successive reductions will retain and weigh exactly the reduced sample. The weights of the reduced sample shall be about 1 kilo for copra and olives, about 500 grams for all other seeds except small seeds, and approximately 100 grams for small seeds such as flax, sesame and those of the cruciferous plants such as poppy and tomato.

(c) Separation of impurities. The operations shall be conducted under such conditions that there is no appreciable loss of moisture. When a separation is judged necessary, the sample is reduced, the dust separated by screening, and then the foreign bodies remaining with the seed after screening are removed by sorting. The very laborious

sorting of foreign bodies of approximately the dimensions of the seed in small seed samples may be effected on an aliquot which should not weigh less than 10 grams. The weights of the fractions of impurities are obtained and reported.

The chemist may indicate the percentage of inert impurities according to the specifications of the contracts. In this case the proportion obtained above should be diminished by the quantity of seed dust and particles it contains. This quantity will be calculated by taking into account the oil contents of the impurities and the pure seed. It will be subtracted from the quantity of the total impurities. Letting "P" be the percentage of total impurities, "h" their oil content, and "H" the oil content of the pure seed, the percentage, "I", of total inert impurities will be

$$I = P\ (1 - h/H)$$

The chemist may separate, analyze, and study separately the foreign oleaginous seeds, if any are present, according to the specifications of the contracts.

(d) Grinding. The reduced sample, either original or after separation of impurities according to the choice of the analyst, is ground to a fine meal in a mill appropriate to the nature of the seed. The grinding will be done without heating and under conditions which do not cause sensible loss of moisture.

For such materials as copra, for which grinding is always impossible without loss of oil, recourse must be made to grating, either by hand or preferable by use of a mechanical rasp which allows the entire sample to be reduced. If the grating is done by hand, which does not permit the entire sample to be grated, care must be taken to obtain a sub-sample which is as representative as possible. The dimensions and colors of the different pieces of copra should be taken into account in sub-sampling.

(e) Determination of moisture. The determination is made on the well mixed or grated sample, except for small seeds containing drying or semi-drying oils. These latter are dried without previously grinding.

Five g. (± 0.5 g.) are weighed into a tared metal crystallizing dish (preferably of aluminum), 7 cm. in diameter and 3 to 4 cm. high. The sample should be weighed to 1 milligram.

The use of a vacuum oven is recommended. If one is not available, the dish and sample are placed in an air oven regulated to 103° C. ± 2° and in which the temperature is as uniform as possible. After 3 hours in the oven the dish is allowed to cool in a desiccator and is then weighed. The heating, cooling, and weighing are repeated with one hour heating periods until the loss observed between two weighings is 5 mg. or less.

The percentage of moisture is based on the lowest dry weight observed and referred to the original sample containing the impurities.

Until the industry is able to furnish regularly a pure hydrocarbon, such as pentane or normal hexane, petroleum ether distilling between 40° and 60° C. and having a Bromine Number less than one will be used as the extraction solvent.

As soon as possible after the sample is ground, 10 g. (within 1 g.) weighed to 1 mg. is placed in the thimble of an appropriate extraction apparatus. Continuous extractors are recommended. The extraction flask (A) receiving the extract is previously dried and weighed. Extract for 4 hours. Remove the solvent and weigh the flask and contents to 1 mg. The thimble is removed from the apparatus and placed in a current of air until the major part of the solvent is lost from the meal.

The contents of the thimble are emptied into an iron or bronze mortar and ground as fine as possible after adding about 10 grains of fine silicious sand. The reground meal is replaced in the thimble and extracted for an additional 2 hours, receiving the extract in the same extraction flask (A).

Following the same procedure the meal is again ground in the mortar and extracted for another 2-hour period. However, the extract is received in a fresh dry and tared flask (B).

The major part of the solvent is removed from flasks A and B by by distillation on a boiling water bath.

The last traces are eliminated by heating at a temperature of approximately 100° C., and not exceeding 105° C. The removal of the solvent may be aided by blowing air into the flasks at intervals or by submitting the flasks to vacuum. The heating must not be prolonged for more than 20 minutes. The flask is allowed to cool in a desiccator and weighed. The heating and weighing is repeated in the same manner until two successive weights do not differ more than 10 mg.

The last weight obtained is used to determine the weight of the oil extracted. If the weight of the oil in flask B is not more than 10 mg. the operation is terminated. The weight of the oil in the analytical sample is the sum of the weights of the oil in flasks A and B.

If the weight of oil in flask B exceeds 10 mg., new extractions preceded by fresh grinding should be made until a weight of oil extracted during a 2-hour period does not exceed 10 mg.

It should be verified that the oil extracted is quite clear. If not, the impurities are determined with the aid of petroleum ether and corrections made accordingly.

When the determination of oil is made on a very wet seed the filled thimble is submitted to partial drying to reduce the moisture content to approximately 10% before placing it in the extractor.

When oil is determined in the dust separated from the seed by screening the procedure is limited to a single extraction of 4 hours. The effect of the small error thereby introduced on the oil content of the original sample is negligible, because of the usual small percentage of dust.

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METHODS OF ANALYSIS OF FATS AND OILS

METHOD 2. WATER AND VOLATILE MATTER

By water and volatile matter at 105° C. is meant all material volatile up to 105° C. and the total quantity of uncombined water that is found in the sample of fat or oil.

(1) Determination of water and volatile matter. Twenty g. of the sample are weighed into a tared dish, 8 - 9 cm. in diameter and 4 - 5 cm. in height, preferably one having a flat bottom, and containing a small thermometer. The dish is placed on a sand bath over a small flame and the moisture and volatile matter is driven off while stirring constantly with the thermometer, without exceeding a temperature of 105° C. The heating is discontinued as soon as bubbles of water vapor stop forming. The dish is weighed after cooling. The loss in weight gives the "water and volatile matter" content of the sample.

(2) Determination of water only. Twenty to 100 g. of the sample are weighed into a short-necked, round-bottomed flask. Approximately 100 ml. of xylene and several pieces of pumice are added, the latter to control boiling. The flask is connected to the apparatus shown in the figure by means of a cork stopper. This apparatus consists of a cylindrical graduated tube provided with a stopcock for draining. The tube is connected to a reflux condenser. The flask is heated to boiling and the water carried over is received in the graduated tube. When the distilled solvent becomes clear and when no more water separates, the heating is stopped and the apparatus is allowed to stand long enough for the water to settle so that there is no zone of an emulsion between the water and the xylene.[1]

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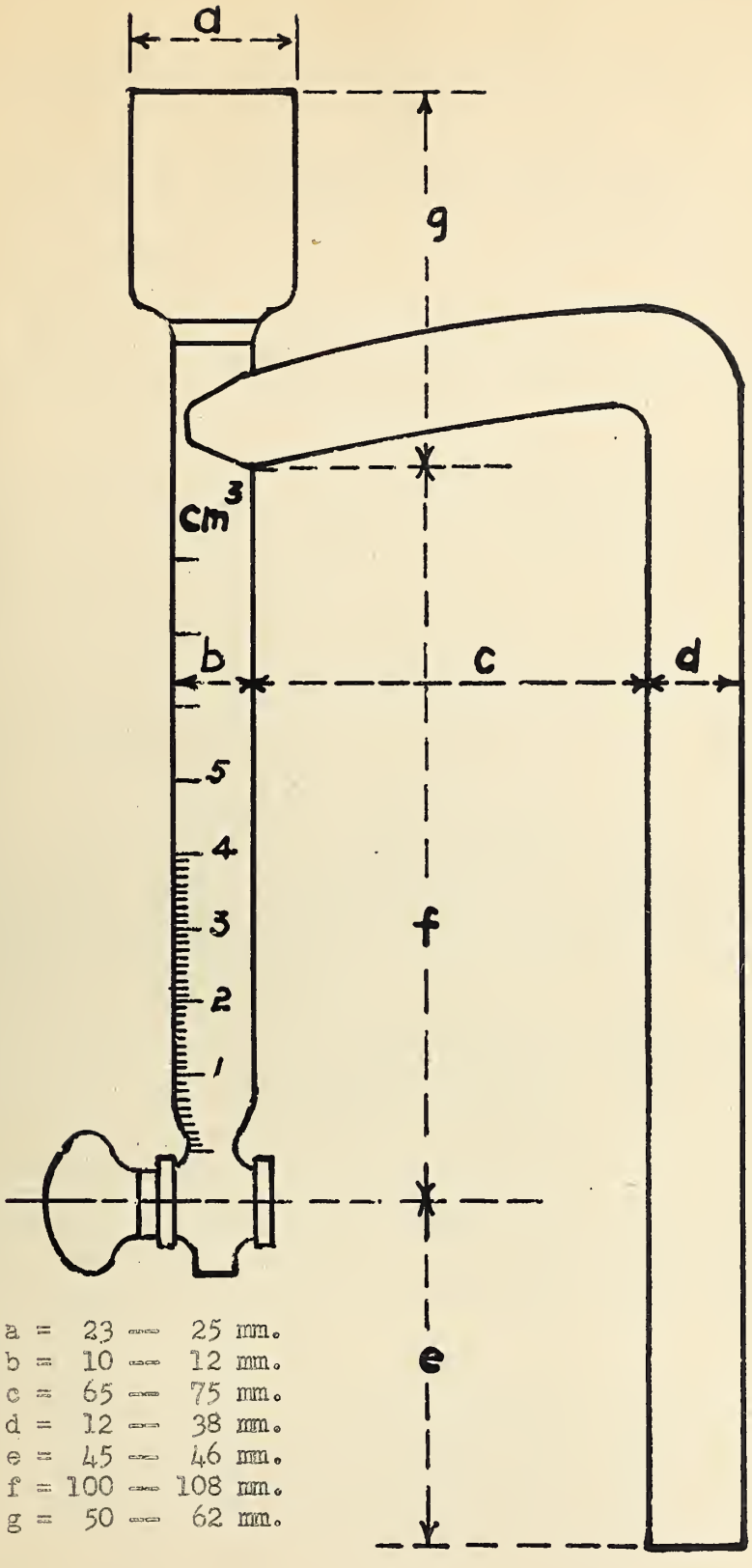
[1] The use of a special apparatus for rapid breaking of the emulsion by centrifugation of the graduated tube is suggested.



a	=	23 —	25 mm.
b	=	10 —	12 mm.
c	=	65 —	75 mm.
d	=	12 —	38 mm.
e	=	45 —	46 mm.
f	=	100 —	108 mm.
g	=	50 —	62 mm.

If drops of water adhere to the sides of the tube, they are detached by heating gently the sides of the tube with a small flame.

The addition of 1 - 2 g. of paraffin or olein is suggested when boiling of the xylene results in foaming.

It is very important that the graduated tube be cleaned carefully of all traces of grease before each determination.

METHOD 3. IMPURITIES

In general, the impurities obtained by use of a volatile solvent represent all the substances not dissolved in the solvent under the conditions of the test and which have not been determined already as water and volatile matter.

From the total weight of these substances may be subtracted the weight of certain of them which according to the terms of the contracts or usage should not be considered as "impurities."

The only three solvents used are:

(a) recently distilled neutral ethyl ether,

(b) petroleum ether (B. P. between 40 and 60° C. and Bromine Number < 1), and

(c) recently distilled carbon tetrachloride.

The choice of the solvent depends on the nature of the fatty material tested and on the nature of the substances which should be considered as "impurities." The choice of solvent may be imposed by usage or by contract.

The impurities in edible fatty materials and in crude fat products destined to become edible after further treatment should be determined with the use of petroleum ether.

Under the conditions of the test described below,

(a) ethyl ether leaves insoluble mechanical impurities such as earth, sand, various debris, etc., inorganic matter, carbohydrates, nitrogenous substances, certain resins, calcium soaps, and alkali soaps;

(b) petroleum ether leaves insoluble mechanical impurities such as earth, sand, various debris, etc., inorganic matter, carbohydrates, nitrogenous substances, certain resins, oxidized acids, lactones, and calcium soaps (dissolving only partially hydroxy acids, their glycerides, and the alkali soaps); and

(c) carbon tetrachloride leaves insoluble mechanical impruities such as earth, sand, various debris, etc., inorganic matter, carbohydrates, nitrogenous substances, certain resins, and calcium soaps. (It dissolves only partially the alkali soaps.)

The calcium soaps are counted as "impurities" unless the contracts between groups state otherwise. In this latter case they are not included as impurities except for the lime which they contain, expressed as CaO.

In the absence of indications to the contrary, the alkali soaps are not included as impurities, except for the bases which they contain expressed as oxides.

The report of the analysis should indicate the solvent used and finally the constituents which are deducted from the impurities.

Procedure. A 20 g. sample of the melted but not dried fatty material (several drops of water are added with stirring if the sample has been previously dried) is treated with 200 ml.[2] of the chosen solvent in a stoppered erlenmeyer flask. The whole, after shaking, is allowed to remain at a temperature of about 20° C. for about 30 minutes if ethyl ether or petroleum ether is used and for 12 hours if carbon tetrachloride is the solvent used.

The mixture is then filtered on a dry tared filter. The filter is washed carefully with small quantities of the solvent until the filtrate is free of fatty substances. The washings are limited to the amount of solvent strictly necessary.

The filter is dried in the oven at 105° C. to constant weight. The increase in weight gives the amount of "impurities" present.

Notes

(1) In the presence of a fatty material containing soaps and where soaps should not be included as "impurities" except for the bases they contain, the insolubles are removed from the filter and boiled in a flask fitted with a reflux condenser with 0.2 N HCl until the soaps are completely decomposed. The fatty material so liberated is extracted in a separatory funnel with the solvent used for the determination of "impurities." After washing with small portions of water to remove the mineral acid, filtering, and evaporating the solvent, the fatty acids liberated from the soaps are weighed. The weight is expressed as anhydrides of the fatty acids and the percentage so obtained is deducted from the impurities.

2/ In certain particular cases the volume of solvent may be increased.

(2) When the residue insoluble in the solvent used contains both calcium and alkali soaps, and when only the calcium soaps should be included as "impurities," it is necessary to incinerate the filter at a low temperature and determine the water-soluble alkali in the ash. The alkali so determined is that of alkali soaps. The amount of combined fatty acids is obtained by using the following equivalent weights for the fatty acid anhydrides:

191 for coconut, cabbage palm, and similar oils,
247 for palm oil, and
273 for all other fatty materials.

The amount of combined fatty acids is deducted from the percentage of "impurities."

(3) In some cases the solution of fatty material may contain, even after filtration, inorganic substances which should be added to the impurities retained on the filter. In such cases, the solvent is evaporated and ash determined on the oil, using the procedure given for the determination of ash.

METHOD 4. ASH

The ash represents the inorganic residue on ashing filtered fatty material. Its percentage should not be added to that of the insoluble impurities, to avoid accounting for certain elements twice. On the other hand, ash may be determined on the purified fatty material after removal of the solvent. In such cases the percentage of ash is added to that of the "impurities."

Procedure. Ten to 15 g. of the fat or oil are weighed into an appropriate capsule. It is heated carefully to the ignition point and allowed to burn spontaneously. To avoid volatilization of the volatile alkali salts, the carbonaceous residue is washed with hot water and the solution filtered on an ash-free filter paper. The filter and the carbon are then burned until the incineration is complete. The incineration is facilitated by adding several drops of peroxide or by calcining in a gentle current of oxygen.

After cooling, the filtrate is returned to the capsule and evaporated to dryness on a water bath. Finally, the whole is calcined.

The ash may be recarbonated if desired by adding ammonium carbonate or water saturated with carbon dioxide.

METHOD 5. ACIDITY

Acidity is the percentage of free fatty acids and may be expressed conventionally, depending on the nature of the oil, as oleic, palmitic or lauric acid, according to the following:

oleic acid, molecular weight 282;
palmitic acid, molecular weight 256; or
lauric acid, molecular weight 200.

If p is the weight of sample used, n the volume of alkali necessary for neutralization, expressed as ml. of normal alkali, the expressions for calculating the acidity, A, are:

$$A \text{ (as oleic acid)} = \frac{n \times 0.282 \times 100}{p},$$

$$A \text{ (as palmitic acid)} = \frac{n \times 0.256 \times 100}{p} \text{ (particularly for palm oil), and}$$

$$A \text{ (as lauric acid)} = \frac{n \times 0.200 \times 100}{p} \text{ (particularly for coconut, cabbage palm and laurel oils).}$$

When the results mention the term "acidity" without indicating how expressed, it is always understood, conventionally, that the acidity is expressed in terms of oleic acid.

The acidity may be expressed also as the "acid number," which is the number of milligrams of KOH necessary to neutralize the free acids in 1 g. of fatty material. This introduces the factor of 56.11, representing the molecular weight of KOH:

$$I\ A = \frac{n \times 56.11}{p}$$

Acidity, being a characteristic of fatty material, should be determined as the percentage of weight of the dried and filtered sample.

Procedure. The fatty material is first freed of water by decantation and filtration on paper, effected at a temperature slightly higher than the melting point of any solid constituents which may have separated from the liquid fat.

Five to 10 g. of the filtered sample are dissolved in approximately 150 ml. of a mixture of equal parts of 95% ethyl alcohol and ethyl ether. The mixed solvent is first neutralized with a 0.1 N solution of alkali.

The solution is shaken and titrated with 0.5 N aqueous or better alcoholic alkali (potassium or sodium hydroxide) in the presence of phenolphthalein. For samples of weak acidity, 0.1 N alkali is used.

Notes

It may be necessary to make special determinations when free or combined mineral acids are present.

The acidity id determined on the sample as received with products containing volatile fatty acids, specifying separately the moisture and calculating the acidity on the basis of the dry, or moisture free, product.

As a point of information, it is recalled that an International Convention decided to express acidity of fatty materials intended for food as ml. of N alkali per 100 g.

METHOD 6. UNSAPONIFIABLE MATTER

Unsaponifiable matter includes the natural unsaponifiable constituents of fatty material (sterols, hydrocarbons), as well as organic substances not volatile at 100° C. (mineral oils) which are foreign to fatty materials but which they may contain.

In general the percentage of unsaponifiable matter should be added, for reduction in price, to the percentages of water and impruities, its determination is effected on the fatty material as received. If otherwise, and it is desired to express the unsaponifiables as percentage of pure fatty material, the percentage is found by calculation, taking into account the determinations of moisture and impurities. In this case the results are noted as being "on the pure fatty material."

Procedure[3/]

(a) With petroleum ether. Five grams of the fatty material are weighed into a flask fitted to a vertical condenser. To it are added 50 ml. of an approximately 2 N solution of potassium hydroxide, in 95% ethyl alcohol. The mixture is boiled for 1 hour. Fifty milliliters of distilled water are then added through the top of the condenser. After mixing and cooling, the contents of the flask are transferred to a separatory funnel. The flask is rinsed several times with a total of 50 ml. of redistilled petroleum ether (B. P. 40 - 60° C., Bromine Number < 1) free of residue. The washings are transferred to the separatory funnel. The mixture is shaken vigorously for one minute in order to insure thorough contact between the petroleum ether and the soap solution. The separatory funnel is allowed to stand and when the two phases have completely separated, the soap solution is drawn off into

3/ The certificate of analysis should mention the method which was used. It would be desirable for commercial contracts to specify the method which should be used.

a second separatory funnel. It is again extracted with a 50-ml. portion of fresh petroleum ether, separated and extracted a third time with 50 ml. of fresh petroleum ether. Emulsions, which are sometimes encountered, may be destroyed by the addition of a small quantity of alcohol or by extraction with a concentrated solution of potassium hydroxide.

The three portions of petroleum ether extract are then combined in a separatory funnel and are washed with three successive 50-ml. portions of 50% alcohol. The petroleum ether solution is transferred to a small flask, the solvent removed by distillation, and the residue dried at 100° C.

For this drying, the flask is placed in a horizontal position in an oven maintained at 100° C. After 15 minutes in the oven the flask is allowed to cool and is weighed. Weighings are made after quarter hour intervals of heating until the loss in weight between two consecutive weighings is less than 0.10%. If this result is not obtained after three periods of drying the presence of unsaponifiable matter foreign to natural unsaponifiable matter is indicated.

When the technique is followed strictly, the unsaponifiable matter obtained is free of soap. To avoid any error which might result from accidental entrainment, the unsaponifiable matter separated is incinerated. If ash remains, its alkalinity is determined with 0.1 N acid in the presence of methyl orange. Each ml. of the 0.1 N acid represents 0.032 g. of potassium soap to be deducted from the unsaponifiable matter as originally determined.

(b) With ethyl ether. Five grams of fatty material is weighed into a 250-ml. flask, and approximately 50 ml. of N alcoholic potassium hydroxide are added. The color of the alcoholic alkali solution should not be darker than straw yellow. Fit the flask to a reflux condenser and heat on a boiling water bath for 1 hour, shaking from time to time.

Remove the flask from the bath and condenser and transfer the the contents to a 500 ml. separatory funnel. Wash the flask several times with water, using a total volume of 100 ml. (Translator's Note. -- Assume the washings are added to the contents of the separatory funnel.)

Rinse the flask with 100 ml. of ethyl ether (D 15° -- 0.720 - 0.724) and pour the ether solution into the separatory funnel. Stopper the funnel and shake vigorously while the contents are still slightly warm. Keep the funnel in a vertical position until the two clear layers of liquid separate.[4]

[4] In the case of a persistent emulsion, caused by too strong an alkalinity of the mixture, several drops of N HCl are added.

Separate the aqueous alcoholic layer into the flask used for the saponification. Transfer the ether layer to a second 500-ml. separatory funnel containing 40 ml. of water. Extract the alcoholic aqueous soap solution twice more, each time with 100 ml. of ethyl ether in the same manner and combine the three portions in the second separatory funnel. If the ethyl ether extracts contain solid substances in suspension, they should be filtered and the filter washed with a little ethyl ether. Swirl the separatory funnel containing the ethyl ether extractions and the 40 ml. of water without violent shaking, and after separation draw off the wash water. Then wash successively with two more 40-ml. portions of water, 40 ml. of 0.5 N aqueous KOH, 40 ml. of water, and again with 40 ml. of 0.5 N aqueous KOH, and again at least twice with 40 ml. of water. Continue the washing with water until the water no longer gives a pink color on the addition of phenolphthalein.

Transfer the ether solution to a tared flask and evaporate to a small volume. Add 6 ml. of acetone and completely remove the volatile solvent from the flask by means of a gentle current of air while the flask is almost submerged and is rotated obliquely in a bath of boiling water. Complete the drying in an oven at 100° C. under the conditions indicated in the method using petroleum ether.

Dissolve the contents of the dried flask in 20 ml. of freshly boiled and neutralized 95% ethyl alcohol and titrate with 0.1 N alcoholic KOH in the presence of phenolphthalein.

If the titration does not exceed 0.1 ml., calculate the proportion of unsaponifiable matter in the fat by dividing the weight of the residue obtained by the weight of the sample and multiply by 100. If the titration exceeds 0.1 ml. the determination should be repeated.

Notes. For each of these methods certain National Commissions recommended the addition of a known weight of fixed oil (approximately 2 g.) to the unsaponifiable matter before oven drying in order to avoid loss of certain volatile unsaponifiables, when the fatty materials being examined contain volatile unsaponifiable constituents, particularly in the case of extracted fats and oils.

METHOD 7. DENSITY

Because of the confusion which sometimes occurs between the terms "density" and "specific gravity" according to the meaning in different countries, and even occasionally within a single country according to available texts, it is emplasized here that the term density at t° designates the absolute density, that is the mass of a unit volume, expressed in grams per cubic centimeter at the temperature indicated. The quantity is indicated by the symbol Dt.

This quantity (Dt) approximates the density with respect to water at 4° C. (d t/4) to within 0.000027, which is within an accuracy not obtained by ordinary precision measurement.

The exact determination of the temperature has considerable importance, as the density of fatty materials varies approximately 0.00068 per degree centigrade. As in the case of refractive indexes, densities are determined on dried and filtered fatty materials and are reported at 20° C. (and eventually at 40°, 60°, ... for materials whose state is ill defined at 20° C.).

In practice the measurements may be made at a temperature t_1 near the temperature of reference t and corrected to the latter as follows:

for $t_1 > t$

$$Dt = Dt_1 + (t_1 - t) \times 0.00068, \text{ and}$$

for $t_1 < t$

$$Dt = Dt_1 - (t - t_1) \times 0.00068.$$

Procedure. Density is determined by use of a pycnometer. After the pycnometer has attained the constant temperature of the ambient medium, it is filled to the top of the capillary tube. The thermometer is introduced and the pycnometer is weighed and the temperature noted.

The density at t°, (Dt), is obtained by use of the following expression:

$$Dt = \frac{c - a}{b - a} \Delta, \text{ in which}$$

a = the weight of the pycnometer,
b = the weight of the pycnometer filled with water at t°,
c = the weight of the pycnometer filled with oil at t°, and
Δ = the density of water at t°, which is obtained from appropriate reference tables.

The approximate value of Dt indicated above can be corrected for the effect of air pressure,

$(Dt) = Dt + 0.0012 (1 - Dt)$, with (Dt) being the corrected value and 0.0012 the density of the air.

For solid fats the determination is conducted as follows: The pycnometer is filled approximately 3/4 of its height with the fat and placed in an oven at the melting temperature of the fat, in order to remove all traces of air trapped in the sample. After cooling, the pycnometer containing the fat is weighed. Water at t° is then added to the top of the pycnometer and the whole is placed in a bath at t° for 1 hour.

The pycnometer is carefully wiped and the weight of the pycnometer, fat, and water is determined.

The density of the fat at t°, (Dt), is then calculated,

$$Dt = \frac{c - a}{(b - a) - (d - c)} \Delta, \text{ with}$$

a = the weight of the empty pycnometer,
b = the weight of the pycnometer filled with water,
c = the weight of the pycnometer and the fat,
d = the weight of the pycnometer filled with the fat and water, and
Δ = the density of water at t°, which is obtained from appropriate reference tables.

The approximate value of Dt for solid fats can be corrected for the effect of air as in the case of liquid fats and oils cited above.

METHOD 8. REFRACTIVE INDEX

The index of refraction of a substance for a determined wave length is the ratio of the sine of the angle of incidence to that of the angle of refraction made by a ray of light of that wave length in passing from air into that substance.

Unless otherwise specified the index of refraction is given for the D line of sodium. The notation n^t always means the index relative to the D line at t° C. If the measurement is made with relation to a radiation X, the notation is n_X^t.

Being a physical characteristic, the index of refraction should be determined on perfectly anhydrous and filtered fatty materials.

Procedure. Any apparatus permitting the measurement of the refractive index may be used. On the other hand the Commission does not recommend any apparatus giving empirical values.

The observations are made for liquid fats at ambient temperature (20° C.) and for solid fats at a temperature above the fusion point but as near as possible to the reference temperature. Exact measurement of the temperature at which the index is determined is necessary.

The sample should fill completely the space between the prisms of the instrument. The observation should be taken after the temperature has become constant, which is in about 5 minutes after the sample has been placed between the prisms.

The accepted reference temperatures are: 20° C. for oils, and 40 - 60 and 80° C. for solid fats and mixtures of fatty acids.

Observations are sometimes made with diffuse light, which is converted to sodium light by an achromatizer. High precision measurements are always made by use of sodium light.

Values observed at t_1, different from the chosen reference temperature t, are converted to that temperature by use of correction factors: F = 0.00035 for oils, and F = 0.00036 for solid fats and fatty acids.

For temperatures lower than the chosen reference temperature, the conversion expression is:

$$n^t = n^{t1} - (t - t_1) F;$$

and for temperatures higher than the reference temperature

$$n^t = n^{t1} + (t_1 - t) F.$$

Example:

n = 1.46991 at 17.5° C., which gives

n^{20} = 1.46991 - 0.00035 (20 - 17.5), and

n^{20} = 1.46904.

Notes. Essential conditions for obtaining comparable values are (a) constant temperature, and (b) perfectly anhydrous fatty materials free from impurities.

In the interpretation of results it is necessary to consider the fact that the presence of free fatty acids greatly lowers the index of refraction.

METHOD 9a. PREPARATION OF INSOLUBLE FATTY ACIDS

Procedure. Weigh approximately 50 g. of homogenized fatty material into an appropriate vessel of convenient capacity (1.5 liters). Place over a small flame and heat to 115 - 118° C.

Then, while stirring and scraping constantly with a metal spatula, add alcoholic KOH (approximately 1/3 the weight of the fat of KOH dissolved in the smallest possible amount of water and 50 ml. of 95% ethyl alcohol).

Mix and scrape the mass in the vessel constantly while heating until the soap is dry enough to form fragments which do not adhere to the spatula under gentle pressure.

Pour 1000 ml. of boiling water over the soap and boil for 45 minutes in order to remove all the alcohol and obtain a clear soap solution.

Remove from the heat and replace the water lost by evaporation with cold water. Pour 70 ml. of sulfuric acid diluted to 25° Baumé (66° Baumé acid diluted with 4 volumes of water) into the soap solution, taking special care that no traces of undecomposed soap are allowed to remain adhered to the sides or bottom of the vessel.

Boil the mixture until the free fatty acids float on the surface as a clear layer.5/

Decant the water as completely as possible and wash the fatty acids with 500 ml. of boiling distilled water (+ 10% NaCl), which is decanted and then a second time with 500 ml. of boiling water (+ 10% NaCl).

Filter on a wet filter and transfer to a vessel. After having separated most of the water by decantation, dry the fatty acids with anhydrous sodium sulfate and filter again. Allow the fatty acids to crystallize for 24 hours in a desiccator where the preparation is intended for the determination of the titer.

Notes. The observations can not be quantitative, but it is essential to observe strictly the proportions of water indicated for the liberation and washing of the acids, in particular from substances such as coconut oil because of the partial solubility of certain constituents in water.

The fatty acids, so prepared, are ready for the determination of titer, molecular weight, or any other physical or chemical property.

If the preparation of fatty acids is for the determination of molecular weight, the last washing is tested for neutrality with methyl orange. It should be neutral if the washings were done well and the decantations were complete.

METHOD 9b. DETERMINATION OF TITER

The titer is the solidification point of the fatty acids. It may be determined by the method of Dalican or by that of Shukoff. The certificate of analysis should indicate the method used.

Method of Dalican. The titer apparatus consists of a test tube, 2.75 cm. inside diameter and approximately 12 cm. long, mounted in a flat stopper which serves as a cover of a wide-mouthed bottle, 10 cm. in diameter and 13 cm. in height. The test tube projects 2 cm. above the stopper.

A precision thermometer, graduated in 1/10 or 1/5 degree and with a range extending to approximately 70° C., is suspended by means of a clamp in the axis of the test tube and extending to within 1 cm. of the bottom of the tube. The bulb of the thermometer is 2 cm. in length and 0.6 cm. in diameter.

5/ The operation should be conducted on a boiling water bath if the fatty material contains glycerides of lauric acid.

To make the measurement of the titer, introduce a portion of the fatty acids (see preparation of insoluble fatty acids), melted at a temperature approximately 10° C. above the presumed titer, into the test tube of the apparatus to fill the tube to a height of approximately 5-1/2 cm. Place the thermometer bulb in the center of the mass of fatty acids and allow to cool without agitation.

The observed temperature first drops rapidly, then more and more slowly, and finally remains constant for 20 to 25 seconds.

The temperature of the surroundings should be approximately 20 to 25° C. less than the presumed value of the titer.

At this moment impart a rapid circular movement to the thermometer, three times to the right and three times to the left, in order to break up the crystals which form in the tube. Replace the thermometer in the center of the tube and observe the temperature.

The temperature, after having dropped during the agitation, rises, attains a maximum, and then drops again. The maximum temperature, which is easy to observe, constitutes the titer.

Repeat the test until values agreeing within 0.2° C. are obtained.

Method of Shukoff. Melt the insoluble fatty acids at a low heat in such a manner that the fusion point is exceeded by only 5 to 10° C. and transfer to the apparatus of Shukoff. Nearly fill the receiver with perfectly dry, melted, and filtered fatty acids. By means of a cork stopper mount a thermometer, graduated in tenths of degrees Centigrade, so that the bulb is in the center of the receiver. When the mass becomes slightly turbid agitate several times and let stand. Note the temperature corresponding to the maximum at which the column of the mercury remains stationary for several seconds. This is the solidification point of the insoluble fatty acids and represents the titer of the sample.

METHOD 10. SAPONIFICATION NUMBER

By saponification number is meant the quantity of potassium hydroxide, expressed in milligrams, necessary to saponify 1 gram of fatty material.

Procedure

Reagents:

(a) Hydrochloric acid, 0.5 N solution, and

(b) Potassium hydroxide, approximately 0.5 N solution in 95% ethyl alcohol. This solution is decanted after standing in a brown or yellow glass bottle closed with a rubber stopper.

Weigh 2 g. of the fatty material into a 200 ml. flask of alkali reistant glass. Add exactly 25 ml. of the alcoholic KOH and boil under reflux for 30 minutes, shaking from time to time. Titrate the hot soap solution with 0.5 N HCl in the presence of phenolphthalein.

Conduct a blank test under the same conditions to titrate the alkali.

Letting C_1 and C_2 be the ml. of 0.5 N HCl solution used in the blank test and in the test with the fatty material, respectively, and p the weight of the analytical sample, the saponification number, I S, is calculated,

$$I\ S = \frac{(C_1 - C_2) \times 28.05}{p}.$$

METHOD 11. IODINE NUMBER

The iodine number of a fatty material is a measure of the degree of unsaturation. In practice it is determined by the absorption of halogens and expressed conventionally in grams of iodine combined with 100 grams of fatty material.

Being a chemical characteristic, the iodine number should be determined in all cases on the dry filtered fatty material.

The methods of Wijs, Hanus and Hübl are retained by the International Commission. The first two are recommended for industrial and commercial analyses. The method of Hübl is still official in certain countries, aside from commercial transactions. The report of results should mention the method used.

In the application of the three methods, the reaction is conducted at a temperature of about 20° C. and is protected from light.

Procedures. For the three methods retained always use a quantity of the reagent such that at the end of the determination there remains halogen in excess at least equal to that absorbed. For the 25 ml. of reagent used the sample weight should be of the order of 32/IJ[6] which gives

1.0 g.	for presumed iodine number of	0 to 30
0.6 g.		30 - 50
0.3 g.		50 - 100
0.2 g.		100 - 150
0.15 g.		150 - 200

6/ For the Hanus method a weight of the order of 25/IJ is recommended.

(a) Wijs' method

Preparation of reagent: Dissolve approximately 9 g. of iodine trichloride (ICl_3) in a liter of a mixture of 700 ml. of glacial acetic acid (at least 99% pure) and 300 ml. of carbon tetrachloride. Determine the concentration of halogen.7/

Then add 10 g. of pulverized iodine and shake until the halogen content, determined in the same manner, is one and one-half times the value first determined. It is important to exceed slightly this limit in order to be sure no traces of iodine trichloride remain. Its presence makes the solution unstable and may cause secondary reactions.

Filter or decant the clear liquid. If desired dilute with glacial acetic acid or with a mixture of glacial acetic acid and carbon tetrachloride until 5 ml. are precisely equivalent to 10 ml. of 0.1 N thiosulfate.

A well prepared solution protected from light and stored in a well-stoppered bottle can be used for several years.

The acetic acid and carbon tetrachloride should be strictly free of oxidizable substances. As a test for them shake 1 or 2 ml. of the acid or the carbon tetrachloride with a little concentrated sulfuric acid and a drop of a concentrated solution of potassium dichromate. No green color should develop.

Determination of iodine number: Take a sample of the fatty material of such size that after the reaction a quantity of iodine will remain unabsorbed at least equal to 70% of the quantity of iodine in the volume of the reagent used.

Introduce the accurately weighed sample into a 300 - 500-ml. glass-stoppered, previously washed and dried flask and dissolve it in 15 ml. of carbon tetrachloride. Then add, preferably from a burette, exactly 25 ml. of the reagent. Stopper, shake gently and place the flask in the dark for 2 hours. (In most cases 1 hour is sufficient. For polymerized or oxidized oils 2 hours are necessary.) At the end of this time add 20 ml. of a 10% solution of KI (free of free iodine and of iodates) and approximately 150 ml. of water. Shake and titrate with 0.1 N sodium thiosulfate, using the starch indicator. Toward the end of the titration it is necessary to shake vigorously.

7/ Determination of halogen: Measure 5 ml. of the solution by means of a pipette or a burette. Add to it 5 ml. of a KI solution (approximately 10%) and 30 ml. of water, and titrate with 0.1 N thiosulfate, using starch as the indicator.

A solution of starch, which can be used for a long time without deterioration, is prepared in the following manner: a mixture of 5 g. of soluble starch with 10 mg. of HgI_2 and 30 ml. of water is poured into one liter of boiling water and boiled for 3 minutes.

Conduct a blank determination at the same time.

Letting b and a represent the volumes of 0.1 N thiosulfate used in conducting the test on the oil or fat and the blank test, respectively and p the weight of the sample, the iodine number, I J, is calculated,

$$I\ J = \frac{(a - b)\ 1.269}{p}.$$

(b) Hanus' method. Dissolve 10 g. of iodine monobromide in 500 ml. of glacial acetic acid, free from alcohol, in a ground-glass stoppered flask, preferable of yellow glass.

Add the analytical sample of the fatty material to a large-mouthed, glass-stoppered 200-ml. flask, previously washed and dried, and dissolve in 10 ml. of chloroform or carbon tetrachloride. Add exactly 25 ml. of the Hanus solution. Stopper, shake, and allow the flask to stand in the dark for 1 hour. Then add 20 ml. of a 10% solution of pure KI free of free iodine and of iodates, approximately 100 ml. of distilled water and titrate the liberated iodine with 0.1 N thiosulfate solution.

Simultaneously conduct a blank test without oil.

The titration and the calculation are done as in the case of the Wijs' method.

(c) Hübl's method. Dissolve 25 g. of iodine in 500 ml. of 96% ethyl alcohol. In another 500 ml. of 96% ethyl alcohol dissolve 20 g. of $HgCl_2$. Filter the latter solution if necessary. Approximately 24 hours before use mix the two solutions. The mixture can not be kept stable for use more than 48 hours.

Introduce the analytical sample into a 500 to 800 ml. glass-stoppered flask. Dissolve the fat or oil in 10 ml. of chloroform or carbon tetrachloride and add exactly 25 ml. of the iodine reagent. Stopper, shake, and leave the flask in the dark for 12 to 24 hours, depending on the value of the iodine number expected. The time of 24 hours applies to drying oils. At the end of this time add 20 ml. of a 30% solution of pure KI free of free iodine and of iodates (if precipitate of mercuric iodide forms add an additional quantity of the KI solution) and 300 ml. of distilled water, and titrate with 0.1 N thiosulfate solution.

Simultaneously conduct a blank determination.

The titration and the calculation of the result are done as in the preceding methods.

METHOD 12. HYDROXYL NUMBER

The hydroxyl number is the weight in mg. of KOH necessary to neutralize the acetic acid which combines on acetylation of 1 g. of fatty material.

Reagents. The acetic anhydride and pyridine used should be pure and dry.

Dissolve 25 g. of acetic anhydride in pyridine in a 100 ml. volumetric flask and make to volume with pyridine. Mix thoroughly by shaking.

The reagent, so prepared, should be kept protected from light, carbon dioxide and acid vapors.

A slight coloration due to the action of light does not affect the value of the reagent. Nevertheless it is preferable to store it in brown glass bottles.

Procedure. Exactly weigh the analytical sample of the fatty material into a 150-ml. flask having a neck 55 mm. in length and 20 mm. in diameter. The size of the analytical sample depends on the hydroxyl number and is indicated in the table given below.

Add the exactly measured volume of the reagent as given in the same table.

Close the flask with a small funnel which serves as a reflux condenser.8/

The flask is placed in a glycerine bath heated to 95 - 100° C. It should be submerged only 1 cm. into the bath. Further, its neck should be protected from heating by a pasteboard disk, perforated by a circular hole through which the neck of the flask is passed.

After an hour remove the flask from the bath, cool and add 1 ml. of distilled water through the funnel9/ and shake to mix.

The mixture becomes warm because of the conversion of the anhydride to acetic acid. In order to complete this reaction and to decompose the fatty acid anhydrides which may have formed return the flask to the glycerine bath for 10 minutes. Then allow it to cool to room temperature.

8/ An acetylation flask connected by a ground joint to a tube forming a reflux condenser may be used. In this case the heating may be accomplished on a boiling water bath. The water to decompose the excess anhydride is added at the top of the condenser. The alcohol for rinsing the condenser and the neck of the flask is added similarly.

9/ The addition of water may produce turbidity. If so, add a little pyridine to make the liquid homogeneous.

Add 5 ml. of neutralized 95% alcohol, rinsing the sides of the funnel and the neck of the flask. Titrate with 0.5 N alcoholic KOH solution in the presence of phenolphthalein (or alkaline blue 6B when the mixture is dark brown).

Simultaneously conduct a blank determination under the same conditions except that no sample of the fatty material is used.

Calculation. Letting a and b represent the ml. of 0.5 N KOH solution used in the titration of the blank and the test with the sample and e the weight of the sample in grams, the calculation of the hydroxyl number is

$$\text{Hydroxyl number} = \frac{28.055 \times (a - b)}{e} + \text{acid number.}$$

Note that the first term of the sum may be negative.

Analytical Sample to be Used

Expected hydroxyl number	Volume of reagent ml.	Analytical sample in grams
10 - 100	5	2.0
100 - 150	5	1.5
150 - 200	5	1.0
200 - 250	5	0.75
250 - 300	5	0.60
	or 10	1.2
300 - 350	10	1.0
- 700	15	0.75
- 950	15	0.50
- 1500	15	0.30
- 2000	15	0.20

METHOD 13. OXIDIZED ACIDS

The fatty materials insoluble in petroleum ether under the conditions specified are conventionally called oxidized acids.

Procedure

(a) Saponification and extraction of unsaponifiables. Treat 5 g. of fatty material as indicated in the method for unsaponifiables by ethyl ether up to the last extraction of the aqueous alcoholic soap with ethyl ether and to the first two washings with ethyl ether.

Pour the aqueous alcoholic solution into a porcelain vessel of of approximately 500 ml. capacity. Add the water used in the first two washings of the ethyl ether.

Boil the solution to remove the traces of ethyl ether and all of the alcohol.

(b) Decomposition of the soaps by hydrochloric acid. Transfer the contents of the vessel to a 500 ml. separatory funnel and rinse the vessel with small portions of water so that the total volume of liquids in the separatory funnel is approximately 150 ml.

Add N HCl in slight excess, 51 ml.

Shake for 2 minutes. Make sure that after shaking no foam remains. Otherwise, add a little hydrochloric acid.

(c) Separation of oxidized acids by petroleum ether. Add 100 ml. of petroleum ether, 35 - 50° C., B. P. range, to the solution in the separatory funnel.

Shake for 1 minute, opening the separatory funnel two or three times to release the pressure.

Allow to stand over night and decant the aqueous acid layer.

Filter the petroleum ether solution on a No. 122 orange filter paper 90 mm. in diameter.

The oxidized acids generally adhere to the sides of the separatory funnel as a red-brown mass.

If they are abundant, remove the potroleum ether by pouring through the top of the separatory funnel in order to prevent stoppage of the stopcock.

Rinse the separatory funnel twice, each time with 25 ml. of petroleum ether which is run through the filter.

Wash the delivery tube of the separatory funnel and the funnel, the filter, and the stem of the funnel with 10, 10, and 5 ml. of petroleum ether, respectively.

Wipe the exterior of the stem of the funnel and the delivery tube of the separatory funnel.

(d) Taking up the oxidized acids in alcohol. Dissolve the oxidized acids, contained in the separatory funnel, successively with 25 ml. and 50 ml. portions of hot ethyl alcohol. Run successively each hot solution through the filter paper.

Then wash the delivery tube of the separatory funnel, the filter, and the stem of the funnel, each with 5 ml. of hot ethyl alcohol. Receive the solutions and washings in a 350 ml. tall form beaker.

(e) Evaporation of the alcohol and weighing of the oxidized acids. Evaporate the alcohol with vacuum under a bell jar. Watch the evaporation and concentrate the solution to a small volume of a few ml.

Transfer the residue to a tared porcelain crucible, 45 mm. in height and 40 mm. in diameter, using small portions of ethyl ether.

The difficulties presented by the evaporation of alcohol are thus avoided. This solvent has a tendency to creep up the sides of the crucible.

Begin the evaporation of the ether in a current of air and finish it on a steam bath. Evaporate until the odor of ether and alcohol has disappeared and an acrid odor is detected.

Place the crucible in an oven at 100° C. for 30 minutes, then cool and weigh.

Continue to heat for half-hour intervals in an oven at 100° C. until a constant weight is observed.

The last weighing, p, represents the weight of the oxidized acids plus the mineral salts entrained with them. In order to estimate these salts, ash the residue to determine the amount of them present. Letting p' be the weight of the mineral salts, the weight of the oxidized acids is p - p'. This is calculated to grams per 100 g. of the fatty substance analyzed.

METHOD 14. POLYBROMIDE NUMBER

The polybromide number is the weight of polybromides obtained under conditions of the test per 100 g. of the fatty material examined.

Recommendations

(1) The bromine and ethyl ether used should be pure and anhydrous.

(2) The bromination should be accomplished without a change in temperature of more than 1 or 2° C. from that of the reaction mixture.

(3) The bromination should be accomplished in a medium previously saturated with polybromides. The medium is prepared by adding a small quantity to it before its use.

(4) The washings should be made at 0° C. with ethyl ether containing in solution 0.06 g. of polybromides per 100 ml.

(5) Finely crushed ice and water are used as a cooling mixture to assure rapid cooling.

Preparation of the fatty acids. Saponify 5 g. of the oil with 25 ml. of N alcoholic KOH solution by boiling under reflux over a small flame for 30 minutes. Toward the end of the heating shake until the medium becomes homogeneous in order to avoid overheating the oil.

Take up the soap solution with 50 ml. of water and transfer to a separatory funnel, using an additional 80 ml. of water in several portions for washing. Add 50 ml. of ethyl ether and decompose the soap with a small excess of approximately N HCl in the presence of methyl orange.

Shake vigorously in order to dissolve the liberated fatty acids. Draw off the aqueous alcoholic layer into another separatory funnel and proceed with a second extraction with 50 ml. of ethyl ether.

Combine the two portions of ethyl ether in the same separatory funnel and wash three times by vigorous shaking with 50 ml. of water containing 10% NaCl.

Transfer the ether solution to a 100-ml. volumetric flask and make to volume with ethyl ether. Add the small quantity of anhydrous sodium sulfate necessary for dehydration. Stopper the flask and shake to mix.

If the bromination is not done immediately, substitute CO_2 for the air in the neck of the flask, restopper and store in a dark place.

Bromination. Bromination is effected with a solution of bromine in ethyl ether prepared by adding 4 ml. of bromine, cooled to 0° C., to 100 ml. of dry ethyl ether maintained at the same temperature. The bromine is added in small portions along the side of the vessel while shaking. The reagent is kept at 0° C. before and during its use.

Tare a flask of about 80 ml. capacity into which has been introduced previously approximately 0.1 g. of polybromides prepared from the same oil or from an oil of the same nature. The polybromides should be reduced to a very fine powder. Add 20 ml. of the ether solution of the fatty acids. Shake to suspend the polybromides. Stopper the flask and place in the ice slurry for 15 minutes, shaking sufficiently to saturate the solution with polybromides.

At the end of this time add 20 ml. of the solution of bromine in small portions, especially at first, shaking constantly and maintaining the flask in the ice slurry so that the temperature of the mixture does not exceed + 1 or + 2° C.

When 2/3 of the bromine solution has been added, the remainder may be added rapidly, with the last portions serving to rinse the sides of the flask.

Stopper the flask and allow it to remain in the ice slurry for 3 hours.

Conduct a blank test in parallel in a similar flask containing the same polybromides to which add 40 ml. of ethyl ether, after having noted the tare, including the polybromides. Place the flask in the ice slurry and shake sufficiently for the ether to become saturated with the polybromides.

Filtration and washing. Filter the solution on a fritted glass crucible surrounded by ice slurry. The filtration is facilitated by use of a very weak suction which should be stopped before completion of each washing to avoid cracking the polybromide cake.

The ether used for washing should be brought to and maintained at 0° C. and should contain 0.06 g. of polybromides in solution per 100 ml.

The polybromides are washed four times, the first two with 20 ml. each and the last two with 10 ml. each of the ethyl ether containing the polybromides specified.

After each addition of the ether, shake the flask vigorously to rinse the walls in order to wash the polybromides thoroughly which adhere to the walls of the flask. Before pouring the ether used for rinsing the flask onto the crucible cool to 0° C. in the ice slurry.

The blank determination is conducted in the same manner.

When working with oils which give small quantities of polybromides the washings may be reduced to three of 10 ml. of the ether each.

Drying and weighing. Place the crucibles and flasks in an oven and raise the temperature progressively to 95 - 100° C. Maintain at that temperature for 30 minutes, cool and weigh.

Note the gain in combined weight, A, of the crucible and flask which served for the test on the oil. Also, note the loss in the combined weight, A', of the crucible and flask which served for the blank determination.

(A + A') represents the weight of polybromides obtained for the sample. This weight is calculated to 100 g. of the fatty material.

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METHODS FOR THE ANALYSIS OF HARD SOAPS

(The methods indicated are applicable only to true soaps.)

METHOD 15a. SAMPLING HARD SOAPS

Reasonable initiative, inspired by the following directions, may be left to the sampler and the analyst.

(1) Divide the material into apparently homogeneous lots according to the external characteristics of the pieces.

(2) Sample separately the lots so divided.

(3) Take the sample from different places in the boxes.

(4) For correct analysis the analytical sample should represent at least the average of 5 pieces.

Pieces should be broken only when weighing more than 250 g. This is done under such conditions that the fractions taken are representative.

METHOD 15b. MOISTURE IN HARD SOAPS

Moisture may be determined by oven drying or by xylene distillation. The latter method can be used only for soaps containing volatile substances insoluble in water. In practice, the results obtained with it are not more exact than the nearest 0.5%.

(1) Method of oven drying. Weigh approximately 10 g. of soap into a tared flat-bottomed dish, 8 - 9 cm. in diameter and 4 - 5 cm. in height containing a small stirring rod.

The soap sample should be prepared for analysis by grating or cutting into very fine slices. If the consistency of the soap necessitates, add a known weight of previously dried pumice or sand.

Place the dish in an oven regulated to a temperature between 100 and 105° C. without exceeding the latter temperature. After an hour, crush the chips, which have swollen, with the rod in such a manner as to pulverize the mass.

Return to the oven until two successive weighings at hourly intervals indicate a loss of weight not more than 0.01 g.

The loss in weight gives the actual moisture content.

Letting p be the weight of the soap sample taken and p' its weight after drying, the water content is

$$\left(\frac{p - p'}{p} \times 100\right) \%.$$

If P_o is the original weight of the piece and P_1 its weight at the time of analysis, the initial moisture content of the soap is

$$\left(1 - \frac{p'}{p} \times \frac{P_1}{P_o}\right) \times 100\ \%.$$

(2) Method using xylene. Weigh 10 - 50 g. of soap into a short-necked flask. Add 100 - 200 ml. of xylene and several pieces of pumice to regulate boiling. Connect the flask to the apparatus shown in the figure (see determination of moisture in fatty materials) by means of a cork stopper.

This apparatus consists of a graduated cylindrical tube with a stopcock for draining. The tube is connected to a reflux condenser. Because of the difficulty of expelling water from soap the distillation should be made rapidly. Heat the flask to boiling. The entrained water is received in the graduated tube. When the distilled solvent is clear and no more water separates, interrupt the heating and allow the apparatus to stand until the water has settled and there is no zone of emulsion.10/

If drops of water adhere to the sides of the tube, they are detached by heating the sides of the tube with a small flame. When boiling of the xylene produces foam, the addition of 1 to 2 g. of paraffin or olein is recommended.

The method is deficient for soaps containing volatile substances soluble in water.

METHOD 15c. FOREIGN SUBSTANCES INSOLUBLE IN ALCOHOL

Foreign substances insoluble in ethyl alcohol may be inorganic in nature, such as carbonates, borates, alkaline perborates, sodium chloride or sulfate, sodium silicate, clays, etc., or organic in nature, such as industrial starch, domestic starch, dextrine, casein, sugar, etc.

Qualitative examination of soaps. Heat approximately 5 g. of the soap with 100 ml. of 95% ethyl alcohol in a flask fitted with a glass tube to serve as a reflux condenser in order to dissolve the small quantities of sodium carbonate and sodium chloride which should be considered as normal constituents of all soaps. A portion of the sample not dissolved is due to the presence of foreign substances in the soap.

10/ The use of a special apparatus permitting the rapid breaking of emulsions by centrifugation of the graduated tube is recommended (Norme B - 6 - 41 de l'AFNOR).

Quantitative examination. Treat 5 g. of previously dried soap with approximately 200 ml. of alcohol (see notes) until solution is complete. Decant the hot solution onto a filter which has been previously dried at 100 - 105° C. and tared.

It is well to agitate the solution so that the impurities will not attach themselves to the glass vessel during the dissolving of the soap.[11] Transfer the undissolved residue quantitatively to the filter by means of small portions of alcohol, and place the receiver containing the alcohol and surmounted by the filter on a sand or water bath. Cover the funnel with a watch glass and heat gently so that the alcohol which distills condenses on the bottom of the watch glass and dropping on the filter eliminates the last traces of soap. Place the filter in a weighing bottle, dry at 100 - 105° C. and weigh. The increase in weight is due to foreign substances present, insoluble in ethyl alcohol. Calculate the weight found to 100 g. of soap.

The residue on the filter may be used to investigate alkali carbonates and to identify other mineral or organic foreign substances.

Notes. The quantitative test is made on previously dried soap, using absolute alcohol in order to separate the total foreign substances. In order to separate only added foreign substances insoluble in alcohol and soluble in water use undried soap and 95% alcohol (by volume).

The report of the results will show the concentration of the alcohol used.

METHOD 15d. TOTAL CRUDE FATTY ACIDS IN SOAPS[12]

Wax cake method. Place 10 g. of soap in a round-bottomed vessel, 11 cm. in diameter, containing a stirrer. Add 100 ml. of distilled water. Place on a boiling water bath. When the solution of the soap is complete, acidify with approximately 10 ml. of 0.2 N H_2SO_4 solution, making certain that there is an excess of acid by testing with methyl orange.

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[11] In spite of all percautions, some insolubles in certain silicate soaps adhere to the glass. After washing with alcohol this portion is taken up in a little distilled water. The water solution is evaporated in a tared crystallizing dish. The residue is dried and its weight is added to that of the foreign substances weighed on the filter.

[12] This method should be considered as a current method and may not be used for arbitration analyses.

The fatty acids separate and come to the surface in a snow-like mass.

Continue the heating, with occasional stirring to shorten the operation, until a layer of clear fatty acids is obtained on the surface of the liquid.

Without cooling, add exactly 20 g. of beeswax (paraffin or olein) which has been carefully washed and dried by heating. When this wax melts, mix it with the fatty acids so that a homogeneous layer is obtained. Allow to cool with the stirring rod in the lip of the beaker.

The supernatant layer solidifies on cooling. When it is sufficiently hard pierce and pour off the underlying water. Replace this water with 100 ml. of boiling water which melts the cake. Wash with this added water and allow to cool so that the cake is reformed.

Pierce the hardened cake and remove the wash water. Then remove the cake, wipe it with filter paper, and finally dry it.

To dry the cake substance heat at 105° C. for 5 minutes in a small tared vessel while stirring with a small thermometer, graduated from 90 to 110° C. and tared with the vessel. Avoid heating in excess of 110° C. because the acids of coconut oil are generally present.

The dried mass is cooled in a desiccator and weighed. Deducting the weight of the vessel, the thermometer and the wax gives the weight of the crude fatty acids contained in the 10 g. sample of soap, that is the weight of the fatty acids plus the unsaponifiables.

Calculate the weight observed to 100 g. of soap.

The results found are increased by 0.50 when the acids contain the fatty acids of coconut and of cabbage palm oils.

METHOD 15e. TOTAL CRUDE FATTY ACIDS IN SOAP[13/]

Ethyl ether method. Dissolve 10 g. of soap in 100 ml. of distilled water by heating in a beaker.

When the solution is complete pour into a separatory funnel, rinsing the beaker with small portions of water.

Add approximately 10 ml. of 0.2 N sulfuric acid solution in order to liberate the fatty acids.

Allow to cool to room temperature and add 100 ml. of ethyl ether.

Shake vigorously for 1 minute and allow to stand.

13/ This method should be used for arbitration analyses.

Transfer the aqueous acid into another separatory funnel and extract with 50 ml. of ethyl ether.

Combine the ether extracts and wash by shaking with water containing 10% NaCl until all mineral acids have been eliminated. Two washings with 50 ml. each should be enough.

Filter the ether solution through a dense paper and receive the filtrate in a tared flask, and wash the filter with small portions of ethyl ether.

Remove almost all the ethyl ether by distillation and dissolve the residue in approximately 20 ml. of neutral 95% ethyl alcohol.

Exactly neutralize with a 0.5 N alcoholic NaOH solution in the presence of phenolphthalein (do not use alcoholic KOH).

Distill the alcohol and dry the residual soap in an oven at 120° C. to constant weight (about one half-hour).

Note the weight of soaps. Deduct from this weight the quantity of NaOH added expressed as (Na - 1). The weight of total hydrated crude fatty acids contained in the hard soap sample is obtained.

METHOD 15f. TOTAL ALKALI IN SOAP

This method determines the sum of alkali bases combined in the form of soap with fatty acids and resins, with carbonic anhydride (carbonates), with silica (silicates), etc., titratable under conditions of the test. The total alkalinity may be determined at the same time as the total crude fatty acids. When the determination of total crude fatty acids is not required and in the cases where the method is deficient, the total alkali is determined by the method of incineration.

Method for the simultaneous determination of total alkali and of total crude fatty acids. Decompose the soap with a quantity in excess of a known strength of N or 0.5 N H_2SO_4. Receive quantitatively the aqueous acids according to the procedure described for the total fatty acids, and titrate the excess H_2SO_4 with N or 0.5 N solution of alkali in the presence of methyl red as the indicator. The results obtained are expressed as Na_2O. Example: Let p be the weight of soap taken for analysis. If n ml. of 0.5 N acid were necessary for the neutralization of the bases present, then:

$$\frac{0.0155 \times n \times 100}{p} = \% \text{ of } Na_2O \text{ (sodium soaps), and}$$

$$\frac{0.0235 \times n \times 100}{p} = \% \text{ of } K_2O \text{ (potassium soaps).}$$

Notes. This method is not applicable when the soap contains calcium carbonate or when it is artificially colored with a coloring substance soluble in water. In such cases the following method should be used.

Method of determination of total alkali by incineration. Weigh 10 g. of the soap into an appropriate vessel. Incinerate with caution, stopping if desired with a black ash.

Take up the ash in hot water and transfer it quantitatively to a 100-ml. volumetric flask. When cool make to volume, mix and filter on a dry filter.

Titrate the total alkali in 50 ml. of the filtrate with N (or 0.5 N) H_2SO_4 in the presence of methyl orange.

Express the total alkali content as Na_2O.

Let p be the weight of the soap incinerated and n the milliliters of normal acid required, the total alkali content as Na_2O in the soap is

$$\% \, Na_2O = \frac{0.031 \times 100 \times 2 \times n}{p}$$

Note. When it is only necessary to determine total alkali, a simple and rapid method, consisting of dissolving 5 g. of soap in 500 ml. of water and titrating the total alkali directly in the presence of phenolphthalein, may be used.

METHOD 15g. TOTAL FREE ALKALI IN SOAPS

Procedure. Dissolve 10 g. of soap on a boiling water bath or over a small flame with constant agitation in 100 ml. of neutral 80% alcohol to which has been previously added a known weight[14] of fatty acids of known molecular weight. For extra pure 72% soaps, 1 g. of fatty acids, corresponding to approximately 3.5 ml. of normal alkali, is sufficient.

After complete solution back titrate the uncombined fatty acids. Let the titration be n' ml. and let n be the ml. required to neutralize the weight of fatty acids added.

(n - n') ml. correspond to the quantity of total free alkali contained in the analytical sample.

The determination is appropriate for soaps containing either sodium thiosulfate, or calcium carbonate.

14/ When a series of tests are being made use a known volume of a freshly prepared alcoholic solution of fatty acid of known titer.

METHOD 15h. ROSIN

As we do not know the accurate mean molecular weights of the rosin and the nature of the fatty acids used, the results of the determination of rosin are only approximate.

Reagents:

(a) Methyl alcohol, 98 - 99%, containing 10 g. per liter of 66° B. sulfuric acid.

(b) 0.2 N alcoholic solution of potassium hydroxide.

Procedure. Approximately 2 g. (called p) of the mixture of fatty acid and rosin to be analyzed are weighed exactly in a 150-ml. flask, which can be attached to a reflux condenser.

Add exactly 20 ml. of the methyl alcohol solution of sulfuric acid. Bring to gentle boil under reflux and continue boiling for 30 minutes. Allow to cool and titrate the liberated acid with the 0.2 N alcoholic potassium hydroxide, using phenolphthalein as the indicator.

Let N be the ml. of alkali necessary.

At the same time make an identical test in which only exactly 20 ml. of the methyl alcohol solution of sulfuric acid is added to the flask.

Let N' be the ml. of alcoholic potassium hydroxide necessary for the blank run.

The percentage of rosin will be

$$\left\{ \frac{(N - N') \times 6.6}{p} - 1.6 \right\} \%.$$

METHOD 15i. DETERMINATION OF CHLORIDES IN SOAPS

Dissolve 5 g. of soap in approximately 50 ml. of distilled water with heat.

Transfer the solution quantitatively into a 200-ml. volumetric flask. Add 5 ml. of concentrated HNO_3 in order to liberate the fatty acids, and then immediately 25 ml. of 0.1 N $AgNO_3$ solution. Place on a steam bath until the fatty acids have completely separated and the AgCl formed has collected in a mass. Cool to room temperature and make to volume with distilled water. Mix by shaking and filter. Reject the first 10 ml. of filtrate. Collect 100 ml. of filtrate and titrate with a 0.1 N solution of ammonium thiocyanate in the presence of 2 - 3 ml. of a 10% solution of ferric alum.

Let n be the ml. of the thiocyanate solution used. The percentage of chloride is

$$[(25 - 2\,n) \times 0.00585 \times 20]\ \%\ \text{as NaCl, and}$$

$$[(25 - 2\,n) \times 0.00746 \times 20]\ \%\ \text{as KCl.}$$